

*Citation:*

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groups and one or more alcoholgroups. It is the combination in one molecule of these two groups, which each delay curdling-time to a certain extent, which increases this power in the case of citrates so strongly (up to 16 times). It is remarkable that the alcoholgroup is as much necessary for the citrate action, as the carboxylgroups.

*Summer of 1911.*

*Delft, Hygienic Laboratory of  
the Technical University.*

**Biochemistry.** — "*The laws of surface-adsorption and the potential of molecular attraction.*" By J. R. KATZ. (Communicated by Prof. J. D. v. D. WAALS). (Introduction).

(Communicated in the meeting of June 1912).

*Exclusion of secondary complications.*

Surface-adsorption or adhesion plays an important part in biological and biochemical processes, but very little is known of its laws. Especially for the solving of some questions about swelling (imbibition) it is desirable to study this phenomenon more closely. Therefore I have made — although the subject really belongs more to physics than to biochemistry — some researches which are only intended as a first introduction to the study of this subject.

The confusion which is still reigning here, comes, I think, for a large part from the fact, that two different things again and again are mixed up: surface-adhesion at substances which have some other action on the adsorbed fluid (formation of a solid solution, swelling, formation of a chemical compound among others) and uncomplicated surface-adsorption. Among the authors who in the course of the 19th century have studied surface-adsorption, not a single one seems to have carried through this distinction as far as might be wished. And even the two latest investigators of this subject, TROUTON<sup>1)</sup> and FREUNDLICH<sup>2)</sup>, still treat the adsorption of water-vapour at glasswool and the adsorption at cotton- or woolfibres, as the same phenomenon; although glass does not take up water between its smallest particles, whereas wool and cotton do this to such an extent that the dimensions of the fibres become perceptibly larger (swelling).

Therefore I think it above all necessary in the experimental study of surface-adsorption, to choose a solid which has no action on the fluid studied. I choose water as the fluid to be investigated,

<sup>1)</sup> Proc. Roy Soc. **77** (1906) en **79** (1907).

<sup>2)</sup> Kapillarchemie.

because of the facility with which its vapour-tensions can be determined with the method to be explained below.

Dr. DAY, Director of the Geophysical Laboratory of the Carnegie Institution in Washington, who has great experience of silicates, advised me to begin with synthetical quartz and synthetical anorthite (Calciumaluminiumsilicate) as adsorbent solids, because these substances, when in mass, certainly do not take up water as a solid solution and have very little inclination to react chemically with water. Dr. DAY had the kindness to have both substances prepared for me in the most pure condition and to have them powdered in a motor-driven agate-mortar as finely as is possible. The material then was sieved through the finest metal sieve (80 meshes per centimeter). In this way the surface of the solid was made as large as possibly can be attained; in this way the best chance was obtained that sufficiently large quantities of adsorbed fluid could be observed in the case of a solid substance which agrees as well as possible with the above requirement.

In order to get an impression how finely divided the substances were, I have suspended a weighed quantity in a known volume of water and have determined with the counting-apparatus for blood-corpuscles of Thoma, how many microscopically visible particles this suspension contained pro m.m<sup>3</sup>. In this way it was found, that 1 mgr. of quartz contains 140 million particles and 1 mgr. of anorthite 120 million. Extraordinarily finely divided powders therefore!

I have determined for both substances the amount of water adsorbed as a function of the vapour-tension. Nine portions of this powder of 1 to 2 gr. each were carefully weighed in crystallizing dishes; these were treated as described below, in order to bring them in the same condition and then were placed above 9 different mixtures of sulphuric acid and water, of which the vapour-tension was known. There they remained until constant weight. Ignition in a porcelain crucible showed the amount of water contained in the material used. Controls showed, that the adsorption at the surfaces of the dishes was too small, compared with the adsorption at the surface of the powder, to have influence of importance.

*Influence of the preliminary treatment of the powder: the adsorbed layer consisting of vapour or of fluid.*

Theoretically there exist two possibilities, when a vapour condenses on the surface of a solid. Either it is condensed as vapour only, or the layer of fluid is formed on the solid.

That indeed different curves are obtained in the case of a solid which is covered with a thin layer of fluid or one by which this layer has been removed by intensive drying, is shown by the experiments of Trouton on the adsorption of water at glasswool <sup>1)</sup>. When the glasswool had been dried during 70 hours at 160° C. in vacuo over phosphorpentoxide (so that we may presume that the adhering waterlayer had been removed) curves were obtained as shown in the subjoined figure. <sup>2)</sup>

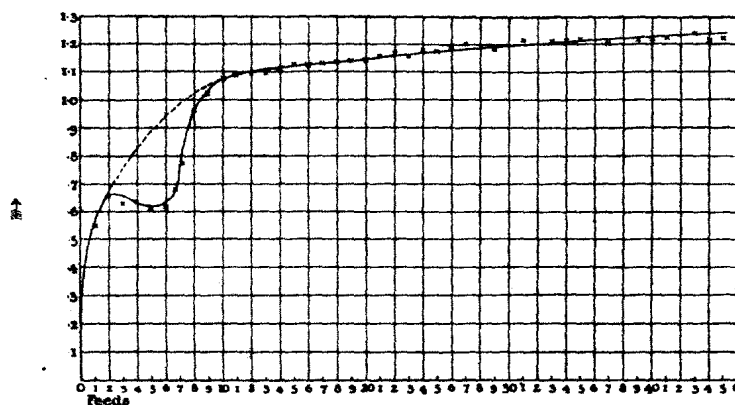


Fig. 1.

The abscissæ represent the amounts of water (in arbitrary units) which are adsorbed at the surface of the glass, the ordinates represent the vapour tension, which is in equilibrium with these. This curve was obtained when going from the driest towards the moister side. The curve rises quickly at the smaller values of the abscissæ and turns its concavity downward, then shows a very curious maximum and minimum and finally quite continuously becomes a line, which in the main seems to agree with the line obtained when a layer of fluid water covers the surface of the glass.

TROUTON has realised this last case only in an impure form, probably because he had to meet the difficulty, that in his experimental technic the curves could only be followed from the driest to the moister side. As driest substance he used glasswool dried at room-temperature over phosphorpentoxide until the vapour tension just had become zero. He then obtained the curve shown below. <sup>3)</sup>

<sup>1)</sup> Proc. Roy. Soc. 79, p. 383—390.

<sup>2)</sup> l. c. p. 385.

<sup>3)</sup> l. c. p. 388.

This curve begins almost horizontally (the first one vertically!) and then has its *convexity* below; with larger abscissae it has its *concavity* below.

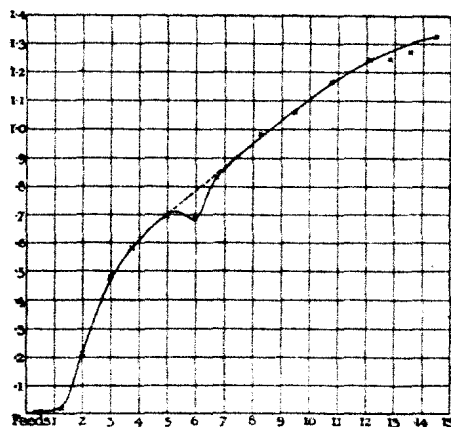


Fig. 2.

The curve still shows however something like a maximum and a minimum. Trouton ascribes this to the fact, that a part of the glasswool is really dry, which means in our conception that a part of it has lost its adherent layer of fluid water. Two different phenomena are thus measured together.

It would be very interesting to know how the curve would be in the other extreme case, viz. when it is certain, that all the glasswool is covered with a layer of fluid water, because, as we shall see, just in this case it can be predicted by approximate calculation how the shape of the curve will be.

#### *Description of my own experiments.*

In order to be sure, that a layer of fluid water covers the particles of the powder, weighed quantities of the powder were placed during several days in a bellglass above a 1% solution of sulphuric acid in water (vapour-tension  $\frac{99}{100}$  of the maximum tension of water)<sup>1)</sup>. Then the dishes were placed over the different mixtures of acid-water till they were of constant weight, in a room which (situated on the north and provided with double windows) had variations of temperature as small as possible.

The following was found as the relation between vapour-tension

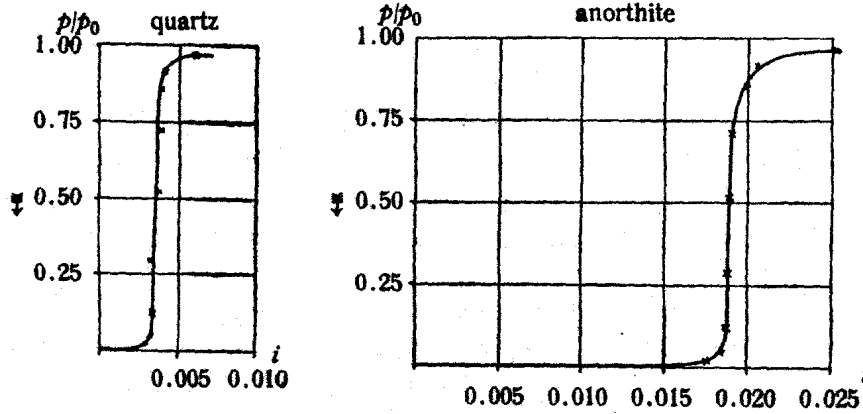
<sup>1)</sup> Pure water would have given too irregular condensations.

and quantity of adsorbed fluid ( $i$  being the quantity of gr. of water, absorbed by 1 gr. of dry powder).

QUARTZ	
$p/p_0$	$i \times 10^3$
0	0
0.020	0.29
0.048	0.31
0.122	0.33
0.306	0.34
0.525	0.39
0.718	0.40
0.857	0.41
0.915	0.42
0.965	0.61

ANORTHITE	
$p/p_0$	$i \times 10^2$
0	0
0.020	1.79
0.048	1.85
0.122	1.87
0.306	1.88
0.525	1.89
0.718	1.91
0.857	1.99
0.915	2.04
0.965	2.53

By graphical representation the following curves were obtained:



Both curves begin with a more or less horizontal part, then have the convexity below, with larger  $i$  first have a flexible point, then have the concavity below; they therefore have the shape of an S.

*Thermodynamical relation between vapour tension and potential of molecular attraction.*

Prof. VAN DER WAALS now called my attention to the fact, that in the following manner an approximate theory of the shape of this

curve can be obtained. When a layer of fluid covers the surface and this is thick enough for us to assign to it the properties of fluid in mass, there exists a simple thermodynamical relation; at least when there is a discontinuous change in density of the layer of fluid and of the coexisting vapour (which is allowed as a first approximation) and when we neglect the very small compressibility of the water.

Then there exists for the vapour tension  $p$ , coexisting with fluid water at a distance  $l$  from the solid wall, the relation:

$$RT \ln \frac{p}{p_0} = k$$

where  $k$  is the potential of the attraction of the solid wall on a distance  $l$ ,  $p_0$  the maximum tension of water at the absolute temperature  $T$ , and  $R$  the constant of gases.<sup>1)</sup>

If the potential of molecular attraction were known, it would be possible to predict how the vapour tension, which is in equilibrium with a layer of fluid of the thickness  $l$ , depends on  $l$ . And because the quantity of adsorbed water  $i$  (in gr. of water pro 1 gr. of dry powder) is related to the surface  $O$  according to the formula

$$l = \frac{i}{O}$$

it would be known at the same time, how the quantity of adsorbed water depends on the vapour tension.

*The potential function of Lord RAYLEIGH and Prof. VAN DER WAALS.*

Prof. VAN DER WAALS proposed, that I should see how far we come with the potential function, which Lord RAYLEIGH and he had adopted in course of their studies about capillarity. They assumed

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<sup>1)</sup> This relation is easily deduced from the general property (VAN DER WAALS—KOHNSTAMM, Lehrbuch der Thermodynamik I, p. 197) according to which in a system, subjected to the action of external forces, the *total potential* of a substance possesses the same value through the entire system. When  $\mu$  is the potential of water vapour,  $\mu'$  the density-potential of water in the point  $l$  (that means the value which the potential of the water would have with the same density but without external forces) and  $k$  the potential of the molecular forces at a distance  $l$  at the solid wall, we have.

$$\mu' + k = \mu.$$

When the compressibility of water can be neglected,  $\mu = RT \ln p_0$ , while  $\mu = RT \ln p$ . It follows from this, that

$$k = RT \ln \frac{p}{p_0}.$$

that the potential on a distance  $l$  from a plain surface (pro unit of weight of adsorbed fluid) is represented by

$$k = -f e^{-\frac{l}{\lambda}}$$

where  $f$  is a large positive constant and  $\lambda$  is a number of the order of magnitude of the diameter of one molecule.

This leads to the relation.

$$RT \ln \frac{p}{p_0} = -f e^{-\frac{l}{\lambda}}$$

or

$$RT \ln \frac{p}{p_0} = -f e^{-\frac{i}{\alpha \lambda}}$$

Discussion of this function gives a curve which begins about horizontally, having its convexity below, then gets a point of inflection; with a still larger  $i$  it has its concavity downward, and finishes about horizontally. So exactly what has been found experimentally. On the relative values of the coefficients  $f$  and  $\lambda$  it depends how large the horizontal beginning will be. One could be in doubt for a moment, whether the formula deduced for a plain surface is valid for the particles of a powder. But as long as these particles are large, compared with the molecular dimensions, an error is made, which is not of importance. And how fine the powders of Dr. DAY may be, the diameter of the particles is always still large compared with the diameter of a molecule.

*Is it possible to determine from experiments on surface-adsorption how the potential function of molecular forces depends on distance?*

Finally an interesting question. We have seen, that the vapour-tension  $p$  and the potential of the molecular forces  $k$  (on a distance  $l$  from the glass-surface) are related to one another according to the formula

$$k = RT \ln \frac{p}{p_0}.$$

If the theory of Prof. VAN DER WAALES is really a sufficient approximation, then it will be possible to calculate  $k$  from the measured vapour-tensions. So we get the relation between  $k$  and the adsorbed quantity of water  $i$ . We should like to know the manner in which



$k$  depends on distance. In order to calculate  $l$  from  $i$ , we must know the total surface of the powder. It is impossible to measure this accurately, but where an estimate is sufficient, we can try to calculate it from the number of particles pro mgr. as described on page 446.

We then assume, that the particles are spheres of equal dimensions and must know the specific gravity of the solids. In this way I have found for the surface of 1 gr.

quartzpowder 3260 cm<sup>2</sup>

anorthitepowder 3150 cm<sup>2</sup>

In this way I have found for the relation between potential and distance the following numbers ( $k$  expressed in cal. pro mol. adsorbed water)<sup>1)</sup>:

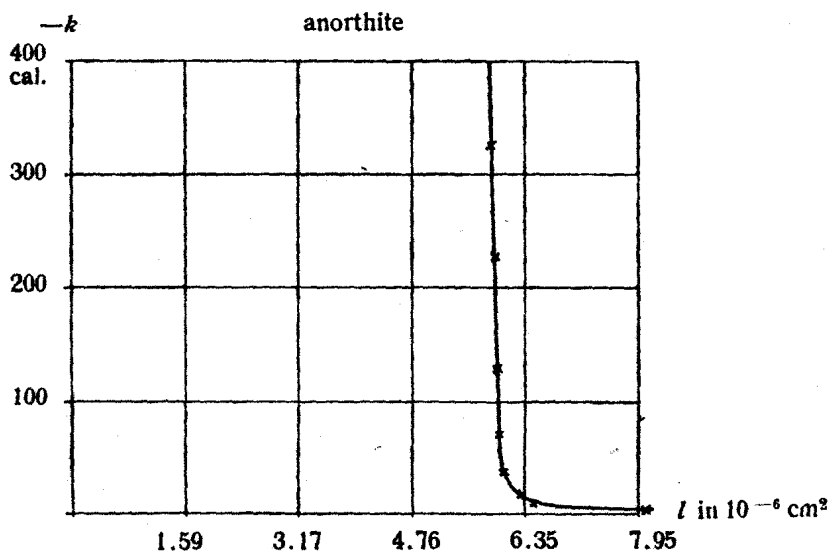
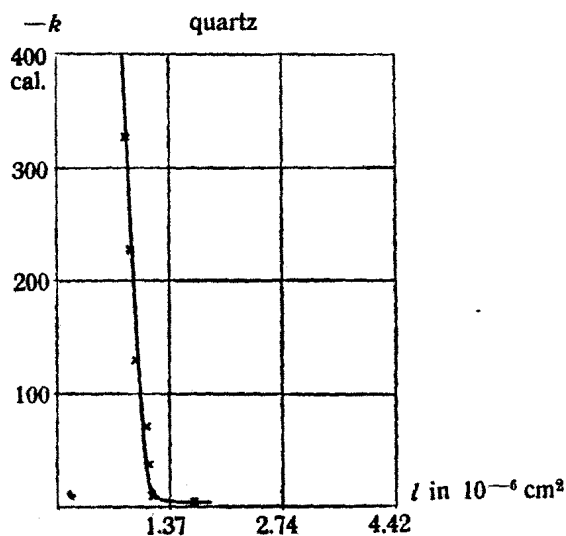
water-quartz (Si O <sub>2</sub> )			water-anorthite (CaAl silicate)		
$-k$	$i$	$l$ in 10 <sup>-6</sup> cm.	$-k$	$i$	$l$ in 10 <sup>-6</sup> cm.
328	0.0031	0.95	328	0.0185	5.87
228	0.0633	1.01	228	0.0187	5.94
128	0.0035	1.07	128	0.0188	5.97
69.8	0.0039	1.19	69.8	0.0189	6.00
36.0	0.0040	1.22	36.0	0.0191	6.06
16.7	0.0041	1.25	16.7	0.0199	6.32
9.62	0.0042	1.28	9.62	0.0204	6.48
3.86	0.0061	1.86	3.86	0.0253	8.03

These tables represented graphically, give the figures shown below; it is, I believe, the first time, that it has been tried to determine *experimentally* the form of the law of molecular attraction. Many assumptions are made about it in theoretical physics, but nobody has so far tried to determine its form by actual measurement. The *shape* of the curve obtained, is not dependent on the exactness of the estimate of the surface of the powder; an error in this estimate can only lengthen or shorten the figure in the direction of the abscissae.

It appears, that the potential diminishes rapidly with increasing distance and has a rather well defined "radius of the attraction-sphere"<sup>2)</sup>. For the size of this radius we find:

<sup>1)</sup> For 17° C.

<sup>2)</sup> We therefore come to the conclusion that the layer of fluid is almost in the whole course of the curve less thick than this radius. The supposition that the fluid has the properties of fluid in mass therefore only is exact as an approximation.



water-quartz  $1.3 \times 10^{-6}$  cm.

water-anorthite  $6.2 \times 10^{-6}$  cm.

while IHMORE<sup>1)</sup> has found in an analogous method (weighing with a very delicate balance the increase of weight of a plain surface of known size in a moist atmosphere)

water-brass  $0.27 \times 10^{-6}$  cm.

water-steel  $0.61 \times 10^{-6}$  cm.

water-nickel  $0.99 \times 10^{-6}$  cm.

water-rock-cristal 0.0 till  $6.0 \times 10^{-6}$  cm.

water-platina 0.0 „  $1.2 \times 10^{-6}$  cm.

water-Jenaglass 0.3 „  $4.0 \times 10^{-6}$  cm.

<sup>1)</sup> Wiedem. Ann. 31, p. 1006—1014. (1887).

Corresponding in order of magnitude with my figures.

There seems to exist no relation with the density of the solid. But it seems that substances with many atoms in the molecule have a larger radius.

Although the results found may still need correction from the fact, that the boundary of the waterlayer and the vapour is not so sharply defined as has been supposed, and because the compressibility of liquid water has been neglected, the results seem interesting enough to call attention to them. Perhaps then some one more competent on this subject, will deduce a less approximate theory. This theory will also have to answer the question, what is the relation between the maximum and the minimum in TROUTON'S curves with the maximum and the minimum in the isotherm of VAN DER WAALS, and if the supposition is right, that it is possible to calculate the maximum and the minimum of the equation of state from the minimum and maximum in TROUTON'S curves.

The importance of these investigations for the problem of swelling (imbibition) will be treated later.

**Meteorology.** — *“The Correlation between Atmospheric Pressure and Rainfall in the East-Indian Archipelago in connection with the 3,5 yearly barometric period”*. By Dr. C. BRAAK. (Communicated by Dr. VAN DER STOK).

(Communicated in the meeting of June 29, 1912).

The regularity of the East-Indian climate renders it eminently fit for clearly revealing weather variations of longer period. There the interest in the weather of next day is quite subordinate to the question whether the coming season will bring much or little rain and since predictions for the immediate future are not wanted, full attention can be paid to those for a more distant future. And this the more so as the circumstances there promise a much better chance of success for a prognosis of the seasons than elsewhere.

That the variations from one year to another are very considerable and an investigation of their character and origin is important, may, perhaps superfluously, be proved by the following summary: (p. 455)

One naturally looks for a relation between the oscillations in the rainfall and the barometric changes of long period.

These variations of the atmospheric pressure are of the same character over an area extending from British India over the Indian